

5 CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the priority of European patent application '00 116 566.1, filed 1<sup>st</sup> August 2000, the disclosure of which is incorporated herein by reference in its entirety.

10 FIELD OF THE INVENTION

15 The present invention concerns new lipid modified polyhydroxyl compounds derived from castor oil, there production and use for the formulation of reactive polyurethane-compositions, in particular for coatings, floorings and adhesives.

20 BACKGROUND OF THE INVENTION

Polyurethanes, resulting from the polyaddition of  
25 polyisocyanates and polyhydroxyl compounds, are broadly used in the form of reactive one or two component systems as adhesives, sealing materials, decorative or protective coatings and floorings. In all these applications their resistance against ageing and attack by chemical substances,  
30 such as for example water, are of great importance. For this reason, a high hydrophobicity of the binder is desired in order to reduce the effects of polar chemicals on the coating or the adhesive. In addition to the chemical resistance, in

particular for coatings, aesthetic aspects are of great importance. Therefore, defect-free surfaces are important and for floorings intended for application outside of buildings a resistance against yellowing due to exposition to UV-  
5 radiation is required.

Besides of these requirements directed to the features of the cured products, high reactivity or short curing times at room temperature are important, since thereby the processing times can be shortened and the costs of the  
10 bound money can be reduced. Furthermore, for the applications in building construction, a sufficiently high reactivity of the systems is a necessity for applications at temperatures around 10°C. This is of great importance since in a lot of geographic regions the average of the application  
15 temperatures during a great part of the year is in this range.

It is known for a long time that because of its high hydrophobicity castor oil is a very suitable polyol for two component polyurethane systems. Thereby castor oil is  
20 often used mixed with other polyols. By epoxydation and thereon following cleavage of the ring with glycols, castor oil and other plant oils can be reacted to as well hydrophobic polyols, that are suitable for the application in two component polyurethane systems. The patent documents WO  
25 96/06123, US 5,512,655 and DE 4308097 describe such polyols. EP 0 798 325 describes a further polyol that is obtained by reaction of castor oil with aromatic polyesters.

Castor oil and the derivatives thereof (such as ricinoleic acid, methylricinoleate, 12-hydroxy stearic acid  
30 methyl ester), as well as the above described reaction products, however, all are characterised by relatively low reactivity with regard to isocyanates, due to the steric hindrance of the therein comprised hydroxyl groups. The above

5 derivatives, is possible, the reaction products of the above  
described polyols with aromatic isocyanates, however, have a  
great tendency for yellowing at the exposition to light.  
Furthermore, due to the low reactivity of the secondary  
hydroxyl groups very fast systems for spraying applications  
10 can only be realised in a very restricted scope. Furthermore,  
the secondary hydroxyl groups very often do not entirely  
react with the isocyanates groups. The remaining not reacted  
hydroxyl groups often lead to a much enhanced hydrophilicity  
of the systems and reduce their life-time.

15 Polyester polyols with enhanced reactivity are described in the patents US 4,656,243, US 4,692,384, US 4,894,430, US 5,260,138 and US 5,319,056. These polyols show a sufficient reactivity to enable a reaction with non-aromatic isocyanates at room temperature. In comparison with  
20 the above described polyols, however, they have a much reduced hydrophobicity.

## BRIEF SUMMARY OF THE INVENTION

Hence, it is a general object of the invention to provide lipid based polyols with high hydrophobicity and simultaneously high reactivity.

A further object of the present invention is a  
30 method for the production of such polyols.

Still further objects of the present invention are specific applications of the polymers of the present invention.



R<sub>4</sub> represents a linear or branched alkylene group, in particular neopentylene, and

R<sub>5</sub> = R<sub>4</sub> or an optionally hydroxyl group substituted linear or branched alkylene group that is  
5 different from R<sub>4</sub>, in particular a neopentylene group or a hydroxymethyl substituted ethylene group.

#### DETAILED DESCRIPTION OF THE INVENTION

10 In view of the reaction preferably used for the production of the polyols, usually - in particular starting from esters of fatty acids - a mixture of compounds of formula (I) is obtained, for example mixtures that comprise  
15 such compounds of formula (I), in which R<sub>4</sub> stems from the polyol and R<sub>5</sub> either from the polyol or from the alcohol of the ester of the fatty acid used as starting material.

Due to their high lipid portion and the primary  
hydroxyl groups, the inventive polyols combine a high  
20 reactivity with a high hydrophobicity. Said polyols therefore are especially suitable for use in combination with aliphatic isocyanates in order to produce light-fast polyurethane compositions, and in combination with aromatic isocyanates  
25 for the production of polyurethane compositions with high reactivity and high weather-proofness. The inventive polyurethanes, i.a. because of the high readiness of the polyol to react, are characterised by excellent mechanical properties. Furthermore, the obtained binders are characterised by excellent compatibility with themselves and  
30 with the filler systems usually used in polyurethane compositions, thereby enabling the production of systems with superior aesthetics.

Optionally, water formed during final esterification can be removed by adding an entrainer, in particular neopentyl glycol.

Furthermore, the production of the binders of the present invention is especially simple and cheap, since the reaction of the lipid part bound hydroxyl groups with the anhydride, in spite of the low reactivity of the lipid part bound hydroxyl groups, is complete and proceeds at relatively low temperatures. The such obtained half esters can selectively be reacted with polyhydroxyl compounds, such as glycols, resulting in the formation of primary hydroxyl groups.

The production is e.g. made in that at least one fatty acid comprising at least one secondary hydroxyl group, or at least one ester of such a fatty acid, or mixtures thereof are reacted with a slight excess of at least one anhydride of a dicarboxylic acid, in particular a cyclic 1,2-dicarboxylic acid, at 150°C to 200°C for about forty minutes. Preferred lipid components are ricinoleic acid and castor oil. Preferred ratios of the mixture of dicarboxylic anhydride to hydroxyl groups of the lipid component are 0.7 : 1 to 1.5 : 1, particularly preferred are ratios of 1.05 : 1 to 1.1 : 1. Reasonably, the reaction is performed in the presence of esterifying catalysts. Suitable catalysts are for example usual esterification catalysts, such as e.g. zinc acetate, zinc oxide, antimony trioxide, esters of titanate, such as isopropyl titanate, tetrabutyl-0-titanate, esters of zirconic acid in concentrations of 0.1 to 0.5 % of the reaction composition. Suitable dicarboxylic anhydrides are anhydrides that lead to stable half esters. Such dicarboxylic anhydrides are in particular anhydrides of cyclic 1,2-dicarboxylic acids, especially preferred cycloaliphatic dicarboxylic anhydrides. In the scope of this

invention cyclic 1,2-dicarboxylic acids are carboxylic acids that have acid groups at adjacent carbon atoms of a cycle.

Examples for anhydrides that are usable in the scope of the present invention comprise hexahydrophthalic anhydride,

- 5 succinic anhydride, glutaric anhydride, methylhexahydrophthalic anhydride, tetrahydrophthalic anhydride, endomethylenetetrahydrophthalic anhydride (Nadig-anhydride) and the derivatives thereof, the liquid mixtures of tetrahydrophthalic anhydride and hexahydrophthalic anhydride and
- 10 cycloaromatic dicarboxylic anhydrides such as phthalic anhydride. Especially preferred for the production of light-fast systems is pure hexahydrophthalic anhydride, or hexahydrophthalic anhydride liquefied with tetrahydrophthalic anhydride, and/or succinic anhydride.

15 In a next step, at least one polyhydroxyl compound is added to the reaction mixture in a ratio of hydroxyl groups to carboxylic acid groups of 1.8 to 2.2, and a further esterification is performed during about two hours at 230°C - 250°C. Preferred polyhydroxyl compounds are

- 20 neopentyl glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol. Also suitable are trimethylolpropane, trimethylolethane, trimethylolmethane, pentaerythritol, diethylene glycol, tripropylene glycol, 1,2-propanediol, isomers of 1,4-butanediol, isomers of 1,5-
- 25 pentanediol, isomers of 1,6-hexanediol, dipropylene glycol, dimethylolpropionic acid, 1,4-cyclohexanedimethanol and isomers, 1,4-bis(2-hydroxyethoxy)cyclohexane, decamethylene-glycol, norbornyleneglycol, 1,4-benzenediethanol, 2,4-
- 30 dimethyl-2-ethylenehexane-1,3-diol, 2-butene-1,4-diol, trimethylolethane, trimethylolpropane, ethoxylated trimethylolpropane, trimethylolpropane monoallylether, trimethylolhexane, 1,2,4-butanetriol, pentaerythritol, dipentaerythritol, pentaerythrit, ethyleneglycol,

diethyleneglycol, dipropyleneglycol. The above mentioned polyhydroxyl compounds can be used alone or as mixtures.

Finally the reaction mixture is cooled. Said reaction mixture can than be used without further  
5 purification.

The inventive polyester polyols are especially suitable for use as component or constituent of a component in two component polyurethane coatings and polyurethane adhesives. Such two component systems with e.g. hexa-  
10 methylenediisocyanate(HDI)-cyclotrimerisate as curing agents are very well suitable as light-fast coatings.

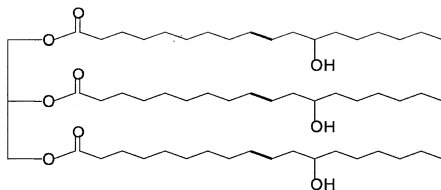
A further object of the present invention are two component polyurethane coatings or two component polyurethane adhesives wherein the resin component contains or consists of  
15 an inventive polyester polyol and the curing component contains or consists of a curing agent on isocyanat basis, for light-fast coatings preferably hexamethylenediisocyanate(HDI)-cyclotrimerisate.

The reaction starting from castor oil and  
20 hexahydrophthalic anhydride (HHPA) followed by neopentylglykol (NPG) is shown in the following schema, whereby in the final product, besides of the fully esterified products represented in the second step furthermore fully esterified diglycerides and triglycerides can be present.

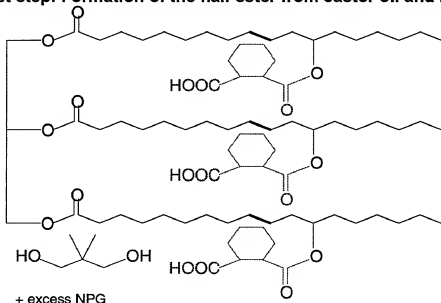
25 In the scheme, the double bound within the fatty acid group is only marked as bold print.



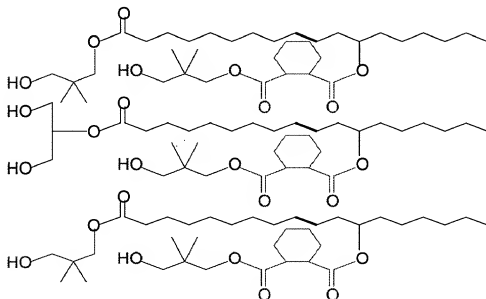
# Castor oil



## 1st step: Formation of the half ester from castor oil and HHPS



**2nd step: Full esterification of the half ester with NPG**



**Examples**

Example 1:

To a laboratory reactor with stirrer and distillation head, 940 g castor oil of quality "first pressing", water content of at most 0.25 %, were added. With stirring, 420 g hexahydrophthalic anhydride that were liquefied in a drying oven at 40°C to 60°C were added to said castor oil. Then 4 g zinc acetate were added as esterification catalyst and the mixture was heated to 180°C within 20 minutes and with further stirring. The half ester formation between castor oil and hexahydrophthalic anhydride was then controlled at 180°C by measuring the increase of viscosity (measurements with cone and plate viscosimeter at 23°C). After about forty minutes of reaction time, the mixture reached a viscosity of 22'400 mPas.

320 g neopentylglykol and 320 g trimethylol-  
propane were added to said batch and a final esterification  
was performed during about 1 ½ hours at 245°C to 250°C.  
During the reaction, about 70 ml condensate were removed by  
5 distillation. After cooling and bottling of the batch, a  
polyester polyol with the following specifications was  
obtained:

Aspect:	yellow, clear, viscous liquid
10 KOH-value:	295
Hydroxyl equivalent:	190 g/eq.
Water content:	0,1 %
Viscosity (23°C)	10'600 mPas

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Example 2:

To a laboratory reactor with stirrer and  
distillation head, 920 g castor oil of quality "first  
20 pressing", water content of at most 0.25 %, were added. With  
stirring, 320 g succinic anhydride in powder form were added  
to said castor oil. Then 4 g esterification catalyst  
(antimony trioxide) were added and (in order to avoid too  
extensive sublimation of succinic anhydride in the reactor)  
25 the mixture was slowly heated to 170°C within 20 minutes and  
with further stirring for half-ester formation. 720 g  
neopentyl-glykol were added to said batch and a final  
esterification was performed during about 2 hours at 240°C.  
During the final esterification, about 80 ml distillate with  
30 a high content of neopentylglycol were collected. After  
cooling and bottling of the batch, a polyester polyol with  
the following specifications was obtained:

Aspect: yellow, clear, viscous liquid  
KOH-value: 261  
Hydroxyl equivalent: 215 g/eq.  
5 Water content: <0,1 %  
Viscosity (23°C) 1'500 mPas

10 Example 3:

As described in Example 1 a half-ester synthesis was first performed, starting from 960 g castor oil, 440 g liquefied hexahydrophthalic anhydride and 4 g esterification catalyst.

15 Then about 480 g neopentylglykol and 120 g of granular pentaerythritol propane were added and a final esterification was performed during about 1 ½ hours at 245°C to 250°C. While neopentylglykol readily dissolved, pentaerythritol remained undissolved until about 220°C. At  
20 the end no bubble formation due to condensate cleavage (water) could be observed anymore. During cooling, at about 210°C, again about 5 ml distillate were removed under vacuum in order to improve the drying, such that a total of 76 ml distillate were collected. After cooling and bottling of the  
25 batch, a polyester polyol with the following specifications was obtained:

Aspect: yellow, slightly turbid viscous liquid  
30 KOH-value: 261  
Hydroxyl equivalent: 215 g/eq.  
Water content: <0,1 %  
Viscosity (23°C) 10'000 mPas

Example 4:

First a half-ester synthesis was performed as described in Examples 1 and 3, starting from 1000 g castor oil, 440 g liquefied hexahydrophthalic anhydride and 4 g esterification catalyst.

Then 280 g neopentylglykol and 280 g granular pentaerythritol are added and a final esterification is performed during about 1 ½ hours at 245°C to 250°C. While neopentylglykol readily dissolved, pentaerythritol remained undissolved until about 220°C. At the end no bubble formation due to condensate cleavage (water) could be observed anymore. During cooling, at about 210°C, again about 7 ml distillate were removed under vacuum in order to improve the drying, such that a total of 70 ml distillate was collected. After cooling and bottling of the batch, a polyester polyol with the following specifications was obtained:

Aspect:	yellow, viscous liquid with medium turbidity
KOH-value:	280
Hydroxyl equivalent:	200 g/eq.
Water content:	<0,1 %
Viscosity (23°C)	34'000 mPas

Example 5:

To the reactor, 840 g ricinoleic acid of quality Edenor RI 90 of Henkel (hydroxyl value 159, acid number 180), were added. With stirring, 440 g hexahydrophthalic anhydride that were liquefied in a drying oven at 40°C to 60°C were added to said ricinoleic acid. Then 4 g esterification

catalyst (zinc oxide) were added and the mixture was heated to 180°C within 20 minutes and with further stirring.

- 340 g neopentylglykol and 400 g trimethylol-propane were added to the above described batch and a final esterification was performed during about 1 ½ hours at 245°C to 250°C. At the end, no bubble formation due to condensate cleavage (water) was observable in the batch anymore. During the final esterification, a total of about 120 ml condensate was obtained. After cooling and bottling of the batch, a polyester polyol with the following specifications was obtained:

Aspect:	yellow, clear, viscous liquid
KOH-value:	274
15 Hydroxyl equivalent:	205 g/eq.
Water content:	0,1 %
Viscosity (23°C):	12'000 mPas

- 20 While there are shown and described presently preferred embodiments of the invention, it is to be distinctly understood that the invention is not limited thereto but may be otherwise variously embodied and practised within the scope of the following claims.

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